II. "The Passive State of Iron and Steel. Part III." By Thos. Andrews, F.R.SS.L. and E., M.Inst.C.E.

Received April 23, 1891.

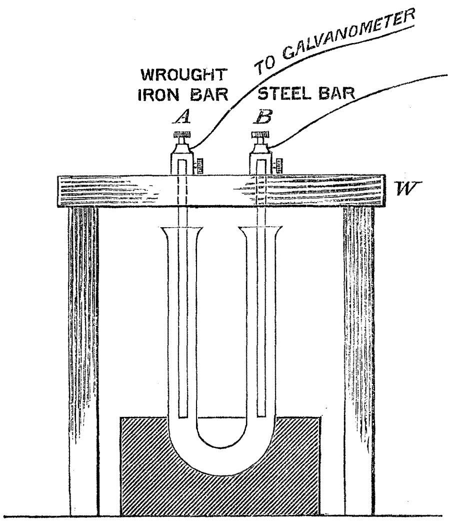
Series V, Set 1.

Relative Passivity of Wrought-iron and various Steel Bars, and the Influence of Chemical Composition and Physical Structure on their Passive State in Cold Nitric Acid.

The author is not aware that any previous experiments have hitherto been made showing the relative passivity of the various kinds of steel compared with wrought iron, or the influence of the chemical composition and physical structure of such metals on their passive condition in nitric acid.

The passive state of iron or steel may have hitherto been regarded by many as a sort of fixed property pertaining to iron and steel alike, when immersed in cold, strong nitric acid. The following experiments were made to investigate if the passivity was of an universally static character, or whether it varied with the chemical composition and general physical structure of the metal and, if so, to what extent. For convenience, this part of the investigation was divided into two parts, one portion of the observations, Set 1, being made on drawn rods of metals of known chemical composition and structure, and the other, Set 2, of experiments constituting a study of the relative

Fig. 5.



passivity of various steel and iron plates of known but varied composition, &c. The experiments of Set 1 were made on bars of the various steels selected from the author's standard samples. The

Table VI.

Time from commencement of experiment.	Current between polished "passive" wrought-iron and steel bars in cold nitric acid 1·42 sp. gr. Electro-chemical position of the wrought iron positive, except where otherwise marked N (negative). E.M.F. in volt.					
	Column 1.		Column 2.	Column 3.		Column 4.
	Soft cast steel with wrought iron.		Hard cast steel with wrought iron.	Soft Bessemer steel with wrought iron.		Tungsten steel with wrought iron.
	Set No. 1.	Set No. 2.	Set No. 3.	Set No. 4.	Set No. 5.	Set No. 6.
seconds						
0	0·000					
30	0·013	0·022 N	0·004 N	0·017	0·016	0·070 N
minutes						
1	0·005	0·022 N	0·016 N	0·022	0·017	0·074 N
3	0·005 N	0·022 N	0·020 N	0·030	0·024	0·073 N
5	0·007 N	0·028 N	0·023 N	0·034	0·032	0·071 N
10	0·011 N	0·026 N	0·022 N	0·034	0·034	0·070 N
20	0·012 N	0·025 N	0·020 N	0·031	0·034	0·065 N
30	0·013 N	0·023 N	0·023 N	0·028	0·032	0·061 N
40	0·013 N	0·019 N	0·020 N	0·024	0·029	0·060 N
50	0·013 N	0·017 N	0·019 N	0·023	0·026	0·059 N
hours						
1	0·013 N	0·014 N	0·019 N	0·020	0·024	0·056 N
$1\frac{1}{2}$	0·012 N	0·011 N	0·020 N	0·017	0·019	0·055 N
2	0·011 N	0·008 N	0·020 N	0·014	0·016	0·054 N
$2\frac{1}{2}$	0·007 N	0·005 N	0·019 N	0·012	0·013	0·052 N
3	0·004 N	0·001 N	0·018 N	0·012	0·013	0·052 N
$3\frac{1}{4}$	0·002 N	0·000	0·018 N	0·011	0·013	0·051 N
$3\frac{1}{2}$	0·000	0·001	0·017 N	0·011	0·013	0·050 N
4	0·002	0·004	0·016 N	0·011	0·012	0·049 N
5	0·006	0·007	0·013 N	0·011	0·011	0·049 N
7	0·016	0·012	0·006 N	0·011	0·011	0·048 N
12	0·037	0·018	0·006	0·012	0·011	0·048 N
18	0·052	0·026	0·017	0·013	0·012	0·047 N
20	0·058	0·030	0·023	0·013	0·013	0·047 N
22	0·064	0·033	0·028	0·014	0·015	0·048 N
24	0·070	0·036	0·033		0·016	0·065 N
26	0·078		0·035			
29	0·085		0·042			
30	0·088		0·047			
38	0·098		0·058			
40	0·107		0·060			
43			0·065			
45			0·071			
47			0·090			

bars were cold drawn through a wortle, and were therefore different in physical structure to the rolled plates used in the second series of the experiments. An idea of their general properties will be obtained on reference to Part II, Tables IV and V. A polished bar, $8\frac{1}{4}$ inches long, 0·310 inch diameter, of the steel to be tested was placed in the wooden stand W (fig. 5), along with a polished wrought-iron bar of equal size, and the pair were then immersed in $1\frac{1}{4}$ fluid ounce of nitric acid 1·42 sp. gr., contained in the U-tube, the bars being in circuit with the galvanometer. The immersion was continued for the periods stated, and with the electro-chemical results given on Table VI.

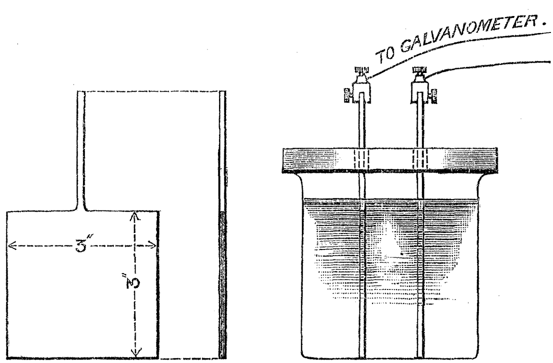
The wrought-iron bars used in each experiment were cut from one longer polished rod, so as to afford a fair comparison of the relative passivity of the various steels, compared with the wrought iron and also with each other. The results are the average of numerous experiments in each case.

Series V, Set 2.

Relative Passivity of Wrought-iron and various Steel Plates in Cold Nitric Acid sp. gr. 1·42.

In the following series of observations, the metals experimented upon consisted of plates of rolled wrought iron, rolled steels made by the Bessemer, Siemens-Martin, or crucible cast-steel processes, and they were of the chemical composition given on Table VII. Each plate was 3 inches square, by $\frac{1}{8}$ inch thick, = total area of exposure, 19·5 square inches including edges, brightly polished all over, and had a long thin strip left on the top side (see fig. 6), for convenience

Fig. 6.



of attaching to the galvanometer connexions. The whole of the wrought-iron plates, used as elements with the various steel plates,

Table VII.

Chemical Analysis of the Wrought-iron and Steel Plates used in the Experiments.

Description.	Combined carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Iron (by difference).	Total.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Wrought iron (Wortley best scrap) ...	none	0·392	0·034	0·270	0·194	99·110	100·000
Soft cast steel	0·460	0·074	0·025	0·210	0·184	99·047	100·000
Hard cast steel	1·407*	0·121	0·056	0·080	0·360	97·976	100·000
Soft Bessemer steel..................	0·150	0·015	0·111	0·064	0·540	99·120	100·000
Hard Bessemer steel	0·510	0·068	0·113	0·087	1·153	98·069	100·000
Soft Siemens steel	0·170	0·071	0·117	0·077	0·627	98·938	100·000
Hard Siemens steel	0·720	0·080	0·102	0·143	1·239	97·716	100·000

* By combustion. The terms "soft" and "hard" relate only to difference of percentage of combined carbon, and not to their having undergone annealing or hardening processes.

Table VIII.

Time from commencement of experiment.	Current between bright "passive" wrought-iron and steel plates in cold nitric acid 1·42 sp. gr. Electro-chemical position of the wrought iron positive, except where otherwise marked N (negative). E.M.F. in volt.					
	Soft cast steel with wrought iron.	Hard cast steel with wrought iron.	Soft Bessemer steel with wrought iron.	Hard Bessemer steel with wrought iron.	Soft Siemens steel with wrought iron.	Hard Siemens steel with wrought iron.
minutes.						
1	0·020	0·071	0·017 N	0·076	0·031	0·065
5	0·032	0·074	0·005	0·079	0·017	0·064
15	0·038	0·073	0·013	0·086	0·024	0·061
30	0·040	0·067	0·012	0·098	0·038	0·064
40	0·048	0·062	0·012	0·107	0·048	0·064
50	0·049	0·059	0·011	0·104	0·053	0·064
hours.						
1	0·047	0·055	0·011	0·103	0·053	0·064
2	0·047	0·061	0·007	0·109	0·034	0·062
3	0·048	0·060	0·000	0·103	0·013	0·061
4	0·047	0·060	0·013	0·098	0·065	0·066
5	0·048	0·058	0·019	0·121	0·007 N	0·060
6	0·050	0·052	0·007 N	0·106	0·022 N	0·056
8	0·038	0·053	0·011 N	0·104	0·037 N	0·059
9	0·040	0·054	0·011 N	0·107	0·034 N	0·058
15	0·053	0·061	0·024 N	0·086	0·017 N	0·055
18	0·060	0·055	0·030 N	0·077	0·008 N	0·056
20	0·050	0·054	0·038 N	0·077	0·007 N	0·058
22	0·040	0·060	0·028 N	0·079	0·007 N	0·061
24	0·038	0·060	0·023 N	0·077	0·007 N	0·064
26	0·046	0·064	0·017 N	0·065		0·064
28	0·049	0·065	0·013 N	0·061		0·062
30	0·050	0·073	0·017 N	0·061		0·066
32	0·049	0·071	0·028 N	0·061		0·070
40	0·052	0·067	0·016 N	0·064		0·084
45	0·050	0·077	0·015 N	0·070		0 090
50	0·046	0·077	0·018 N	0·070		0·088
54	0·046	0·077	0·017 N	0·071		0·086
56		0·078	0·016 N	0·071		
66		0·078	0·017 N			
72		0·067				

were cut from one larger wrought-iron plate and were thus practically of uniform composition, thus ensuring an accurate comparison of the relative passivity of the wrought iron compared with the different types of steels, and at the same time indicating relatively the influence of varied composition and structure on the passivity of the different classes of steel under observation. In each experiment, a polished wrought-iron plate and a polished steel plate were firmly placed in two small holes drilled through a thick plate-glass cover;

the cover holding the two plates was then carefully placed closely over a porcelain vessel containing 15 fluid ounces of nitric acid sp. gr. 1·42, the plates being fully immersed in the acid, and the protruding shanks of the bars connected in circuit with the galvanometer. The electro-chemical effects observed were then taken in the usual manner, and the results are given on Table VIII.

At the conclusion of each experiment on Table VIII, the nitric acid, though quite colourless at first, was found to be of a yellowish-brown colour. A small deposit of fine black carbonaceous-looking matter was noticed at the bottom of the tank surrounding the wrought-iron bar in each set of these experiments.

The hard Siemens-Martin steel plate and the wrought-iron plate, instantly after withdrawal from the acid, showed nearly their original bright polish, with the exception of a few fine streaks or markings on the wrought-iron plate, indicating that the latter metal had been rather more acted upon than the steel plate, the hard Siemens-Martin steel plate presenting a slightly dull-greyish aspect. Somewhat similar results were observed on withdrawing the soft cast steel, hard cast steel, soft Bessemer steel, and hard Bessemer steel series of plates from the nitric acid.

The hard cast steel plate when taken out showed a dull lustre much removed from its original bright polish, but there were no other signs of its having been acted upon. The wrought-iron plate connected with it was bright on withdrawal from the liquid and but very slightly marked.

General Remarks.

It has been necessary to give in modified detail the effects observed during the periods of experimentation recorded on the Tables, Parts I, II, and III, so as to convey an accurate intimation of the method and nature of the research, and a brief *résumé* of some of the principal results and conclusions arrived at by the author up to the present time may now be given.

Firstly.—The experimental observations of Part I, Series I, indicate that the influence of magnetisation on the passive state of steel rods in cold nitric acid sp. gr. 1·42 is not very great, but it was detectable with the delicate galvanometer and by the sensitive electro-chemical method pursued by the author in the investigation.

The effect of magnetisation is more marked in warm nitric acid, and when the iron is in a powdered state, as shown in the independent and separate experiments of Messrs. Nichols and Franklin on passive powdered iron in warm nitric acid, previously alluded to in Part I, by whom it was shown that the temperature of transition from the passive to the active state was very materially lowered by powerful magnetism; their experiments also indicate that the passive state of

powdered iron cannot be fully overcome, even under strong magnetic influence, until a temperature of about 51° C. is reached.

Secondly.—The author's experiments of Part I, Series II, at higher temperatures confirm those of Part I, and further tend to demonstrate the influence of magnetisation in somewhat lessening the passivity of steel, showing that even previous to the critical temperature point of transition from the passive to the active state, magnetised steel bars were rather less passive in warm nitric acid than unmagnetised ones.

Thirdly.—The results in Part II, Series III, show that the passivity of both unmagnetised wrought iron and unmagnetised steel in nitric acid sp. gr. 1·42 is considerably and proportionately reduced as the temperature of the acid increases, until the temperature point of transition from the passive to the active state is reached at a temperature of about 195° F., and it was also found that the wrought iron was less passive in the warm nitric acid than cast steel; see also remarks at foot of Diagram I, in Part II.

Fourthly.—The results of the observations of Part II, Series IV, indicate that Scheurer-Kestner was to some extent in error in regarding the passivity of iron as not dependent on the greater or less degree of saturation of the acid. The author's experiments herein recorded have shown that the passivity of the metals employed, viz., wrought iron, soft cast steel, hard cast steel, soft Bessemer steel, and tungsten steel, was very materially increased with the concentration of the nitric acid, and it was also observed that wrought iron was much less passive in the nitric acid of less concentration than most of the steels, the soft Bessemer steel being found about equal in passivity to the wrought iron under the conditions of experimentation. A reference to Table III shows that a considerable amount of E.M.F. was developed between the different metals in every instance, which is a circumstance of much interest in connexion with the passive state of iron and steel.

Fifthly.—The results obtained in Part III, Series V and VI, on the relative passivity of wrought iron and the various steels, soft cast steel, hard cast steel, soft Bessemer steel, hard Bessemer steel, soft Siemens steel, and hard Siemens steel, are of an important character, showing, by the delicate electro-chemical method employed, the powerful influence of difference in chemical composition and physical structure, &c., on the passive state of the metals. Generally throughout this series of experiments it will be observed that the wrought iron was electro-positive to the steels with a considerable E.M.F., amounting in some cases to as high as one-tenth to one-seventh of a volt, the wrought iron being thus shown to be less passive than the steels. In the experiments on the wrought-iron and various steel bars on Table VI, which in course of their manufacture were drawn cold through a wortle, and were hence in a different molecular condi-

tion to the plates (which were rolled hot) experimented upon in Table VIII, it will be noticed that, in several instances with soft cast steel and hard cast steel, the wrought iron did not assume the electro-positive position until two or three hours after immersion in the nitric acid. Subsequently the iron assumed its normal position, and became during the long remaining period of the observations electro-positive to the steels, with a considerable and increasing E.M.F., showing that the wrought iron was becoming gradually very much less passive than the steels. In the case of the soft Bessemer and soft Siemens plates, Table VIII, we have also a similar instance of these peculiar and temporary interchanges and variations of relative passivity which are not easily accounted for. In the case of the tungsten steel, Table VI, the wrought iron was steadily in the electro-negative position, hence in the latter instance showing the wrought iron to be permanently more passive than the tungsten steel.

A reference to the experiments on the wrought iron and various steel plates, on Table VIII, shows that the E.M.F. between the passive wrought iron and the various soft steels, which contained less percentage of combined carbon, in circuit in cold nitric acid sp. gr. 1·42, was very considerably less than the E.M.F. under similar conditions between the wrought-iron plates and the different hard steels having a higher percentage of combined carbon. The latter results, therefore, demonstrate the interesting circumstance that steels, of a higher percentage of combined carbon are more passive than those of a lower percentage of combined carbon. It will be observed that the wrought iron was also electro-positive to most of the steels, whether of a higher or lower percentage of combined carbon, which shows that wrought iron may be regarded as generally less passive than steels.

III. "On the Demonstration of the Presence of Iron in Chromatin by Micro-chemical Methods." By A. B. Macallum, M.B., Ph.D. Communicated by Professor H. N. Martin, F.R.S. Received April 23, 1891.

(Abstract.)

The method of isolating what is called chromatin by the histologist yields compounds of fairly stable composition called nucleins, some of which have been shown to contain iron (Bunge and Zaleski). My observations on hæmatopoiesis in Amphibia led me to the conclusion that the chromatin, from which the hæmoglobin of the hæmatoblasts is derived, is an iron-holding compound. Other observations indicated that the conclusion could, possibly, be made of general application, *i.e.*, that iron is present in the chromatin of every cell, animal and

FIG. 5.

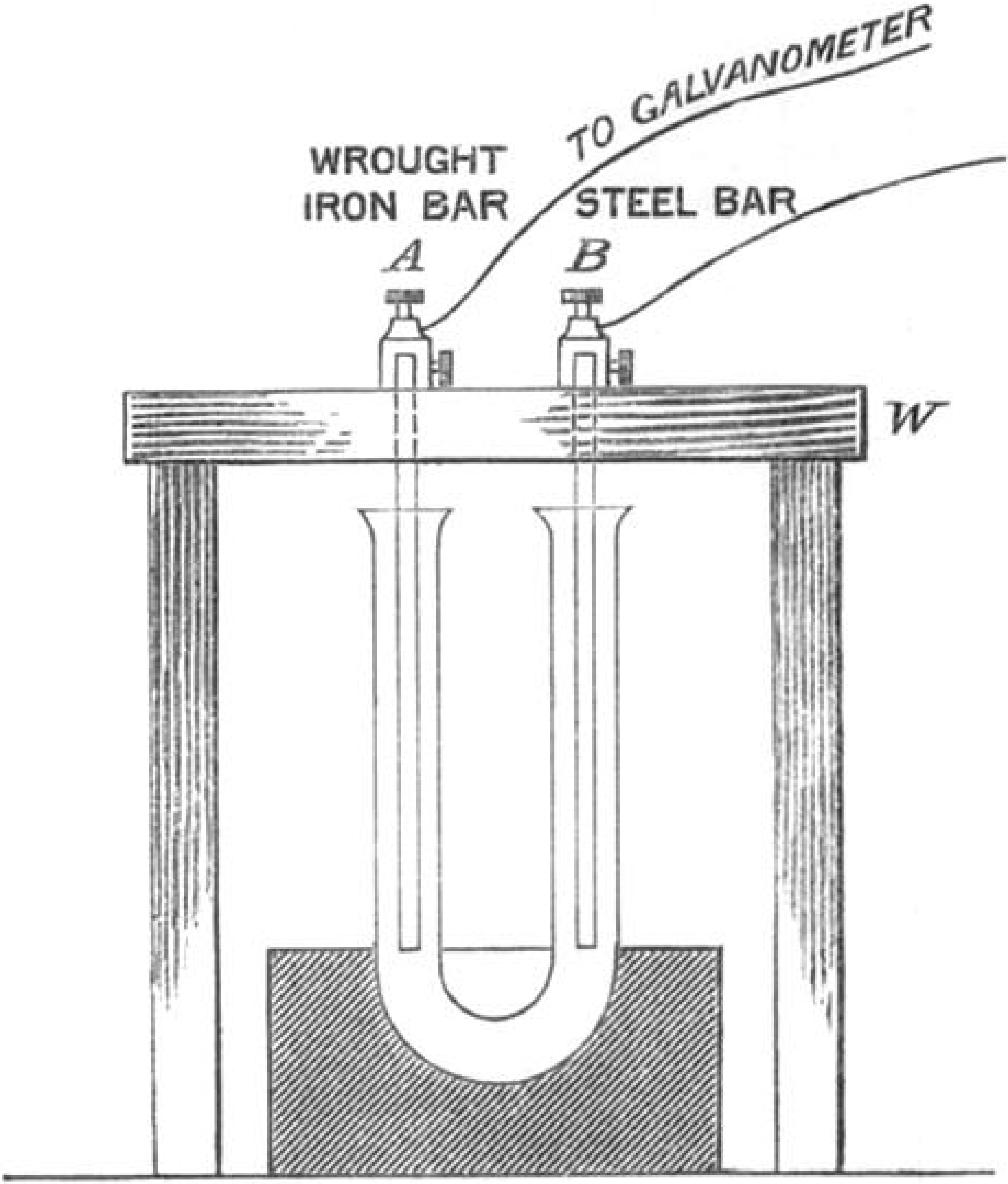


FIG. 6.